Simulations of the polarisation-dependent Raman intensity of photosystem II crystals

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Motivation:

The photosystem II (PSII) molecule complex, which is found in almost every plant, is responsible for the absorption of light and the transport of charge carriers. Linear dichroism measurements [1] suggest involvement of one β-carotene molecule in the photonic induced electron transport. Special carotene Carraf has an exposed position in the reaction center (RC), where the separation of charge happens. The possibility of Raman signal separation was determined by simulations.

Structure of the PS II crystal unit cell:

The unit cell of the photosystem II crystals consists of four dimers containing twelve carotene molecules each. The arrangement of parallel dimer pairs perpendicular to each other suggests an enhancement of the parallel carotene Raman signal. Each dimer contains two RC, where the incoming photons in the photosynthesis are converted into charges.

Simulation conditions:

The crystal structure model of cyanobacterial photosystem II at 2.9-Å resolution [2] was used for the simulation of the β-carotene Raman intensities. The position information of the 40 carbon atoms per carotene molecule are reduced to a direction vector r and the corresponding symmetry vector s. The laser light is propagating in x direction, which is also the rotation axis for polarisation-dependent calculations. The Raman intensities of the two modes vAg and vBg for the individual β-carotene molecules [3] in the unit cell are calculated as follows:

\[
I_r = \left( \frac{\cos(e^{i\phi})}{\sin(e^{i\phi})} \right)^2 \cdot \left| \sum_{i=1}^{n} \left( \frac{\cos(e^{i\phi})}{\sin(e^{i\phi})} \right)^2 \right|^2
\]

Because of the different positions of the carotene molecules in the unit cell, the general Raman tensor \( \mathbf{T} \) has to be transformed individually for each molecule. The transformation is performed by the rotation matrices \( \mathbf{R} \) and \( \mathbf{C} \) around the \( y \) and \( z \) axes with the individual rotation angles \( \beta \) and \( \gamma \). The rotation around the \( x \) axis is in addition to the Raman rotation angle \( \phi \).

Intensity summation of all 96 β-carotene molecules in the PS II crystals with and without the carotenes in the RC:

Results:

Calculated and measured polarisation-dependent Raman intensity of all β-carotene molecules in the PS II crystal unit cell:

Calculated polarisation-dependent Raman intensity of the 3 β-carotene molecules in the PS II crystal RC:

Conclusions:

- good agreement between measured and calculated polarisation-dependent Raman intensities for parallel and perpendicular polarisation
- the intensity for the Bg mode of Carraf is much higher than of Carra and Carra which can help to detect a generated cationic carotene (measurement intended)

References: